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(54) **HIGH-K DIELECTRIC GATE STRUCTURES
RESISTANT TO OXIDE GROWTH AT THE
DIELECTRIC/SILICON SUBSTRATE
INTERFACE AND METHODS OF
MANUFACTURE THEREOF**

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H01L 29/78 (2006.01)

(52) **U.S. Cl.**
USPC **257/411**; 257/412; 257/E29.16

(58) **Field of Classification Search**
USPC 257/E21.192, E21.302
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

| | | | | |
|--------------|------|---------|------------------|-----------|
| 6,284,580 | B1 | 9/2001 | Takehiro | |
| 6,670,249 | B1 | 12/2003 | Pan et al. | |
| 6,790,755 | B2 | 9/2004 | Jeon | |
| 6,919,251 | B2 | 7/2005 | Rotondaro et al. | |
| 7,081,409 | B2 * | 7/2006 | Kang et al. | 438/681 |
| 7,402,472 | B2 | 7/2008 | Lim et al. | |
| 8,158,197 | B2 * | 4/2012 | Gonohe et al. | 427/248.1 |
| 2002/0050644 | A1 | 5/2002 | Matsumoto et al. | |
| 2006/0273411 | A1 | 12/2006 | Triyoso et al. | |
| 2010/0044806 | A1 * | 2/2010 | Hou et al. | 257/412 |
| 2011/0221012 | A1 | 9/2011 | Bu et al. | |

OTHER PUBLICATIONS

NEC Backs Radical Nitridation Over High-k to 70 nm, [online];
retrieved on Aug. 12, 2008]; retrieved from the Internet: <http://www.eetimes.eu/semi/10808635>; 2008.

C.W. Yang et al; "Effective improvement of high-k HF-silicate /
silicon interface with thermal nitridation;" Electronic Letters Mar. 6,
2003 vol. 39 No. 5; pp. 421-422.

J. J. Yu et al; "Direct nitridation of high-k metal oxide thin films using
argon excimer sources;" Electronic Letters Oct. 27, 2005 vol. 41, No.
22; pp. 1-2.

* cited by examiner

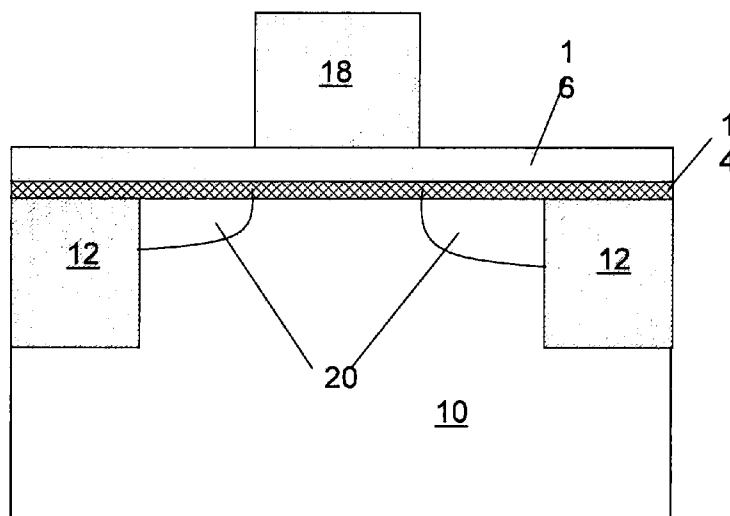
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(57) **ABSTRACT**

Methods for fabricating gate electrode/high-k dielectric gate
structures having an improved resistance to the growth of
silicon dioxide (oxide) at the dielectric/silicon-based sub-
strate interface. In an embodiment, a method of forming a
transistor gate structure comprises: incorporating nitrogen
into a silicon-based substrate proximate a surface of the sub-
strate; depositing a high-k gate dielectric across the silicon-
based substrate; and depositing a gate electrode across the
high-k dielectric to form the gate structure. In one embodi-
ment, the gate electrode comprises titanium nitride rich in
titanium for inhibiting diffusion of oxygen.

8 Claims, 4 Drawing Sheets



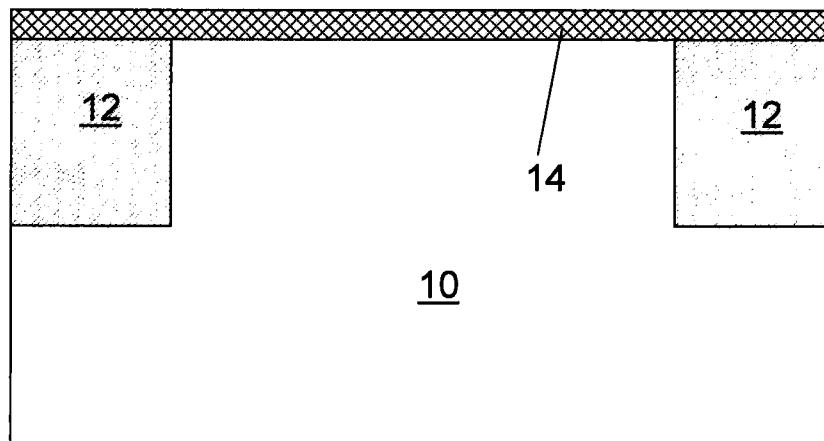


FIG. 1

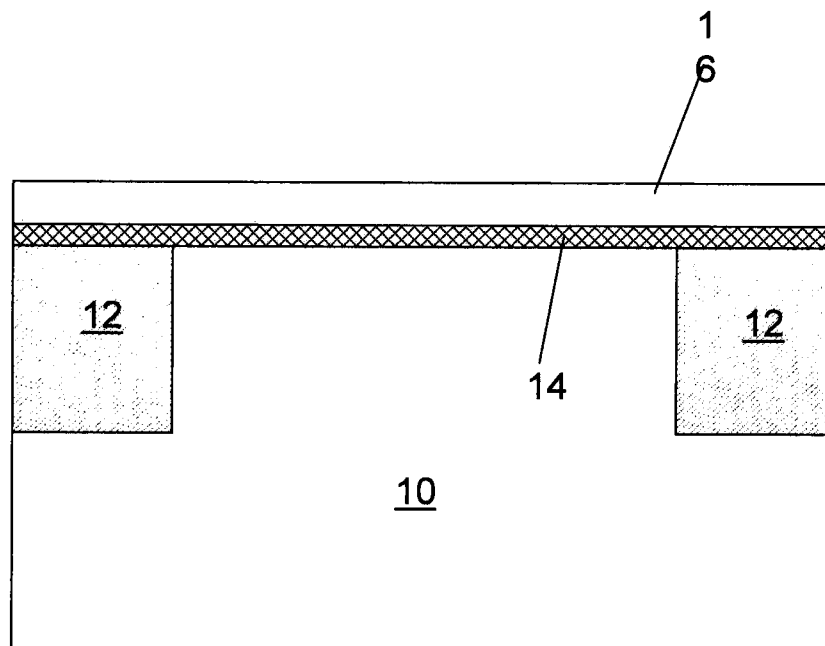


FIG. 2

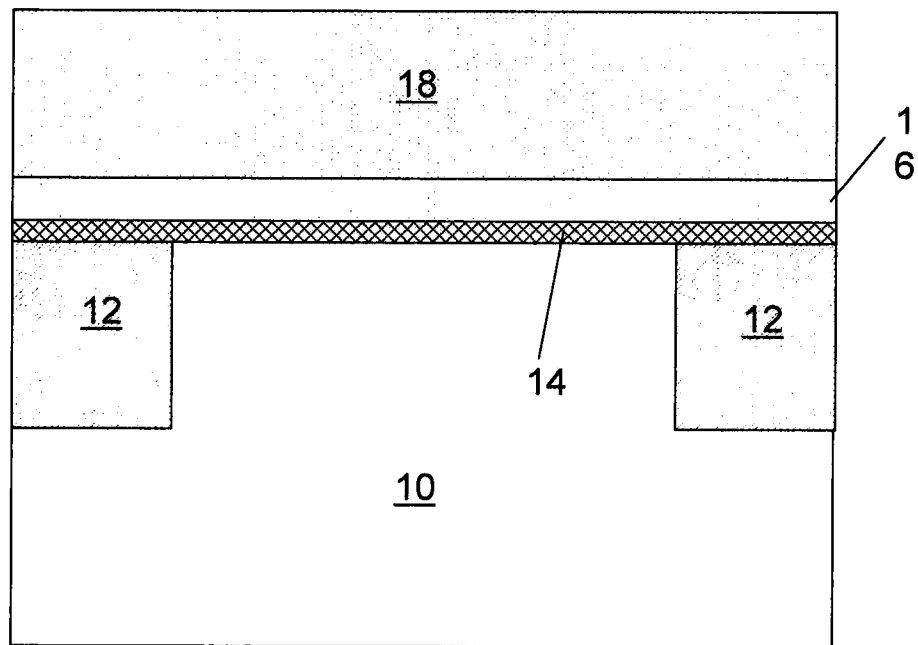


FIG. 3

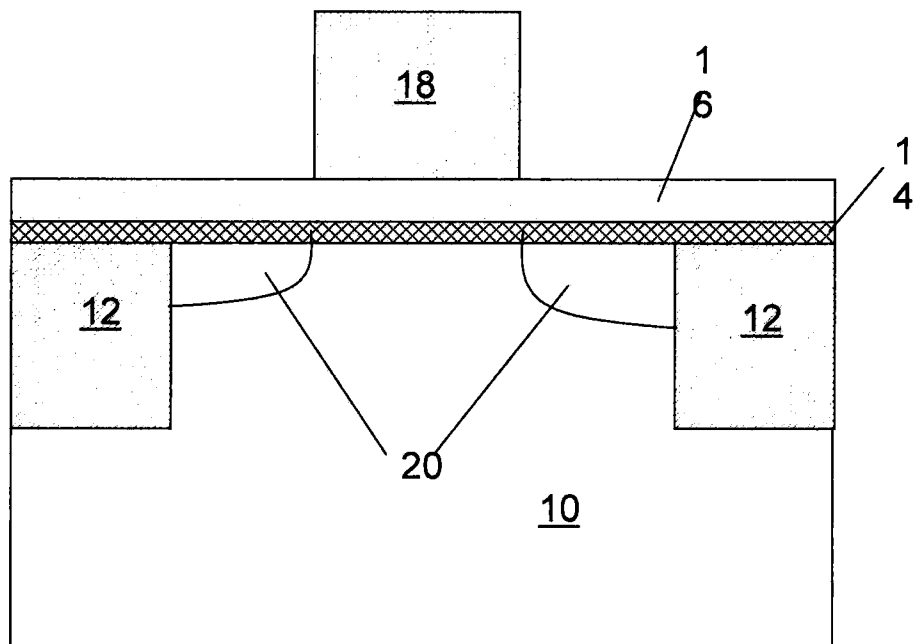


FIG. 4

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HIGH-K DIELECTRIC GATE STRUCTURES RESISTANT TO OXIDE GROWTH AT THE DIELECTRIC/SILICON SUBSTRATE INTERFACE AND METHODS OF MANUFACTURE THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

This application is a divisional of U.S. patent application 10
Ser. No. 12/721,608, filed Mar. 11, 2010 now U.S. Pat. No.
8,318,565, the disclosure of which is incorporated by refer-
ence herein in its entirety.

BACKGROUND

1. Field

This invention relates to integrated circuits, and particu-
larly to fabricating high-k dielectric gate structures having
improved resistance to the growth of silicon dioxide at the 20
dielectric/silicon-based substrate interface.

2. Description of Background

Integrated circuits often employ active devices known as
transistors such as field effect transistors (FETs). A metal-
oxide-semiconductor field effect transistor (MOSFET) 25
includes a silicon-based substrate comprising a pair of impu-
rity regions, i.e., source and drain junctions, spaced apart by
a channel region. A gate electrode is dielectrically spaced
above the channel region of the silicon-based substrate. The
junctions can comprise dopants which are opposite in type to
the dopants residing within the channel region. MOSFETs
comprising n-type doped junctions are referred to as NFETs,
and MOSFETs comprising p-type doped junctions are
referred to as PFETs. The gate electrode can serve as a mask
for the channel region during the implantation of dopants into 35
the adjacent source and drain junctions. An interlevel dielec-
tric can be disposed across the transistors of an integrated
circuit to isolate the gate areas and the junctions. Ohmic
contacts can be formed through the interlevel dielectric down
to the gate areas and/or junctions to couple them to overlying 40
interconnect lines.

The gate dielectric interposed between the channel and the
gate electrode of MOSFETs was once primarily made of
thermally grown silicon dioxide (oxide). Due to the need for 45
integrated circuits having higher operating frequencies, the
thickness of the oxide gate dielectric has steadily decreased to
increase the gate capacitance and hence the drive current of
MOSFETs. However, as the thickness of the oxide gate
dielectric has decreased, leakage currents through the gate
dielectric have increased, leading to reduced device reliabil-
ity. As such, the oxide gate dielectric is currently being
replaced with dielectrics having higher dielectric constants
(k) than oxide, i.e., $k > 3.8$. Such "high-k dielectrics" provide
for increased gate capacitance without the detrimental effect
of leakage current.

MOSFETs that include a metal gate electrode/high-k
dielectric stack suffer from the drawback of experiencing
oxide growth at the interface of the high-k dielectric and the
silicon-based substrate. This oxide growth can occur as a
result of ambient oxygen and/or oxygen in areas of the inte- 60
grated circuit near the MOSFET diffusing to the high-k
dielectric/substrate interface. This oxygen diffusion is more
likely to occur when the integrated circuit is subjected to high
temperatures during anneal steps and/or thermal steps. The
oxide growth can undesirably increase the thickness of the 65
gate dielectric with an oxide having a lower k value than that
of the original gate dielectric. The magnitude of the oxide

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growth is dependent upon the size of the MOSFET and the
nature of nearby structures. Unfortunately, the oxide growth
can undesirably cause a "width effect" in narrow width (or
length) MOSFETs that is often manifested by non-area scal-
ing of the gate leakage current in such small area devices.
Device characteristics of the width effect include a shift in
MOSFET threshold voltage (V_T) and drive current degrada-
tion.

SUMMARY

The shortcomings of the prior art are overcome and addi-
tional advantages are provided through the provision of meth-
ods for fabricating gate electrode/high-k dielectric gate struc-
tures having an improved resistance to the growth of silicon
dioxide (oxide) at the dielectric/silicon-based substrate inter-
face. In an embodiment, a method of forming a transistor gate
structure comprises: incorporating nitrogen into a silicon-
based substrate proximate a surface of the substrate; depos-
iting a high-k gate dielectric across the silicon-based sub-
strate; and depositing a gate electrode across the high-k
dielectric to form the gate structure. In one embodiment, the
gate electrode comprises titanium nitride rich in titanium for
inhibiting diffusion of oxygen.

In another embodiment, a transistor gate structure com-
prises: a silicon-based substrate comprising nitrogen incor-
porated proximate a surface of the substrate; a high-k gate
dielectric disposed upon the silicon-based substrate; and a
gate electrode disposed upon the high-k gate dielectric. In a
particular embodiment, the gate electrode comprises titanium
nitride rich in titanium.

Additional features and advantages are realized through
the techniques of the present invention. Other embodiments
and aspects of the invention are described in detail herein and
are considered a part of the claimed invention. For a better
understanding of the invention with advantages and features,
refer to the description and to the drawings.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

The subject matter which is regarded as the invention is
particularly pointed out and distinctly claimed in the claims at
the conclusion of the specification. The foregoing and other
objects, features, and advantages of the invention are apparent
from the following detailed description taken in conjunction
with the accompanying drawings in which:

FIGS. 1-4 illustrate one example of the fabrication of a
MOSFET comprising a high-k dielectric gate structure
capable of resisting oxide growth at the high-k dielectric/
silicon-based substrate interface.

The detailed description explains the preferred embodi-
ments of the invention, together with advantages and features,
by way of example with reference to the drawings.

DETAILED DESCRIPTION

Turning now to the drawings in greater detail, it will be
seen that FIGS. 1-4 illustrate an exemplary embodiment of a
method for fabricating gate electrode/high-k dielectric gate
structures that are more resistant to the growth of oxide at the
high-k dielectric/silicon-based substrate interface. As shown
in FIG. 1, a bulk substrate 10 comprising single crystalline
silicon that has been slightly doped with n-type or p-type
dopants is first obtained. Alternatively, a semiconductor layer
10 can be formed upon an insulation layer (not shown) to
create a silicon-on-insulator structure. Shallow trench isola-

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tion (STI) structures **12** comprising, e.g., oxide, can be formed in the silicon-based substrate **10** on opposite sides of ensuing MOSFET devices to isolate different active areas of the substrate **10**.

After the formation of the STI structures **12**, a nitridation process can be performed to incorporate nitrogen into the silicon-based substrate **10** and the STI structures **12** proximate their surfaces to form interfacial layer **14**. The nitrogen can be introduced at a dosage greater than about 5×10^{14} atoms/cm² to ensure that the resulting interfacial layer **14**, which includes strong silicon-nitrogen (Si—N) bonds, provides adequate protection against the growth of oxide (SiO₂) upon the substrate **10**. Examples of suitable nitridation processes include but are not limited to exposing the silicon-based substrate **10** and the STI structures **12** to a nitrogen-bearing plasma or subjecting the substrate **10** to a thermal anneal or to rapid thermal processing in the presence of a nitrogen-bearing gas. The nitrogen-bearing plasma or gas can comprise, for example, nitric oxide (NO), nitrous oxide (N₂O), ammonia (NH₃), nitrogen gas (N₂), or a combination comprising at least one of the foregoing gases. By way of example, the thermal anneal can be performed at a temperature of about 400° C. to about 1050° C., more specifically about 600° C. to about 1000° C., or even more specifically about 700° C. to about 900° C., for a period of about 1 minute to about 60 minutes. Rapid thermal processing (RTP) involves rapidly increasing the temperature of a substrate to a target temperature where it is maintained for a relatively short period of time. In this case, the temperature of the substrate **10** can be increased to a temperature ranging from about 600° C. to about 1200° C., more specifically about 850° C. to about 1150° C., or even more specifically about 950° C. to about 1100° C., where it is maintained for a period of about 1 second to about 5 minutes.

Turning now to FIG. 2, a high-k gate dielectric **16** can be deposited across the interfacial layer **14** by, e.g., sputter deposition, atomic layer deposition, or chemical vapor deposition. As used herein, the term “high-k dielectric” refers to a dielectric having a dielectric constant, k , greater than about 4.0, which is higher than the k value of oxide. Examples of suitable high-k dielectric materials include but are not limited to hafnium oxide (HfO₃), hafnium silicon oxynitride (HfSiON), tantalum oxide (Ta₂O₅), aluminum oxide (Al₂O₃), and combinations comprising at least one of the foregoing dielectrics. Without intending to be limited by theory, it is believed that a Si—N—O network forms in the interfacial layer **14** as a result of performing the nitridation process followed by the deposition of the high-k gate dielectric **16**. It is also believed that the Si—O—N network can block the diffusion of oxygen to the silicon-based substrate **10** and thereby reduce the amount of area dependent growth of oxide at the substrate surface. Further, it is believed that the strong Si—N bonds present in this network can contribute to the ability of the interfacial layer **14** to prevent oxygen from migrating through layer **14** and to form a relatively stable layer on the silicon-based substrate **10**.

Next, as shown in FIG. 3, a conductive gate electrode material **18** can be deposited across the high-k gate dielectric **16**. The gate electrode material **18** is desirably optimized to reduce its oxygen content and the diffusion of oxygen through the material **18**. In one embodiment, the gate electrode material **18** is titanium nitride (TiN) rich in titanium (Ti). As used herein, the term “rich in titanium” refers to a material having a greater quantity of titanium than any other component. The deposition of the TiN rich in Ti can be performed using, e.g., physical vapor deposition, atomic layer deposition, chemical vapor deposition, or molecular beam epitaxy. It is desirable to

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form the TiN rich in Ti by physical vapor deposition using a reduced partial pressure of N₂ for reaction with Ti relative to an inert gas such as argon (Ar). For example, the Ar/N₂ mole ratio can be greater than or equal to about 25/20. In alternative embodiments, the gate electrode material **18** could be formed from other conductive materials rich in the metal component such as tantalum nitride (TaN) rich in tantalum or tantalum carbide (TaC) rich in tantalum.

Subsequently, the gate electrode material **18** can be patterned using lithography and an anisotropic etch technique, e.g., reactive ion etching, to define sidewall surfaces of the gate electrode **18**, as shown in FIG. 4. Although not shown, dielectric spacers can then be formed upon the sidewall surface of the gate electrode **18** via chemical vapor deposition of a dielectric followed by an anisotropic etch technique, which etches the dielectric at a faster rate in the vertical direction than in the horizontal direction. Without intending to be limited by theory, it is believed that the presence of the gate electrode **16** comprising TiN rich in Ti in the gate structure affords additional protection against the growth of oxide at the surface of the silicon-based substrate **10** because the gate electrode **16** has a relatively low oxygen content and forms a good barrier to the diffusion of oxygen.

FIG. 4 also depicts the formation of source and drain (S/D) junctions **20** in the silicon-based substrate **10** on opposite sides of the gate electrode **18**. In the case where an NFET is being formed, the S/D junctions **20** can be formed through the implantation of p-type dopants therein. In the case wherein a PFET is being formed, the S/D junctions **20** can be formed through the implantation of n-type dopants therein. While FIG. 4 only depicts the formation of one type of FET, it is understood that both NFETs and PFETs can be formed upon the silicon-based substrate **10** when it is desirable to form a complementary metal-oxide-semiconductor (CMOS) integrated circuit. During the implantation step, the gate electrode **18** and the dielectric sidewall spacers, if present, act as a mask that inhibits dopants from passing into an underlying channel region of the substrate **10**. Examples of n-type dopants include but are not limited to arsenic, phosphorus, and combinations comprising at least one of the foregoing dopants. Examples of p-type dopants include but are not limited to boron, boron difluoride, and combinations comprising at least one of the foregoing dopants. The dopants can be subsequently activated via a thermal anneal process.

The MOSFET formed in FIG. 4 includes a stacked gate structure comprising a nitrogen-incorporated interfacial layer **14** disposed upon the silicon-based substrate **10**, a high-k gate dielectric **16** disposed upon the interfacial layer **14**, and a gate electrode **18** disposed upon the high-k gate dielectric **16**. The gate structure can have a narrow gate width of, for example, about 0.1 micrometer to about 50 micrometers. The interfacial layer **14** can have a thickness of about 0.5 nanometers (nm) to about 2 nm, more specifically about 0.5 nm to about 1 nm. The high-k gate dielectric **16** can have a thickness of about 1 nm to about 5 nm. Moreover, if the gate electrode **18** is a Ti-rich TiN, it can have a thickness of about 1 nm to about 20 nm.

As described above, the gate structure shown in FIG. 4 includes both an interfacial layer **14** comprising Si—N—O between the substrate **10** and the high-k gate dielectric **16** and an optimized gate electrode **18** (e.g., a Ti-rich TiN gate electrode) for improving the resistance of the gate structure to the growth of oxide upon the substrate surface. Consequently, the MOSFET comprising this gate structure is less likely to exhibit characteristics related to width effect such as a shift in V_T and a decrease in drive current.

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As used herein, the terms “a” and “an” do not denote a limitation of quantity but rather denote the presence of at least one of the referenced items. Moreover, ranges directed to the same component or property are inclusive of the endpoints given for those ranges (e.g., “about 5 nm to about 20 nm,” is inclusive of the endpoints and all intermediate values of the range of about 5 nm to about 20 nm). Reference throughout the specification to “one embodiment”, “another embodiment”, “an embodiment”, and so forth means that a particular element (e.g., feature, structure, and/or characteristic) described in connection with the embodiment is included in at least one embodiment described herein, and might or might not be present in other embodiments. In addition, it is to be understood that the described elements may be combined in any suitable manner in the various embodiments. Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs.

While the preferred embodiment to the invention has been described, it will be understood that those skilled in the art, both now and in the future, may make various improvements and enhancements which fall within the scope of the claims which follow. These claims should be construed to maintain the proper protection for the invention first described.

The invention claimed is:

1. A transistor gate structure, comprising:
a silicon-based substrate comprising nitrogen incorporated proximate a surface of the substrate;

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a high-k gate dielectric disposed upon the silicon-based substrate; and

a gate electrode disposed upon the high-k gate dielectric, wherein the gate electrode comprises tantalum nitride rich in tantalum.

2. The transistor gate structure of claim 1, wherein the nitrogen is present in the silicon-based substrate at a dosage of greater than about 5×10^{14} atoms/cm².

3. The transistor gate structure of claim 1, wherein the high-k gate dielectric comprises hafnium oxide, hafnium silicon oxide, tantalum oxide, aluminum oxide, or a combination comprising at least one of the foregoing dielectrics.

4. The transistor gate structure of claim 1, wherein the gate structure comprises a Si—N—O layer at an interface between the silicon-based substrate and the high-k gate dielectric for inhibiting the diffusion of oxygen to the substrate.

5. The transistor gate structure of claim 4, wherein the Si—N—O layer has a thickness of about 0.5 nanometer to about 2 nanometers.

6. The transistor gate structure of claim 1, wherein the high-k gate dielectric has a thickness of about 1 nanometer to about 5 nanometers.

7. The transistor gate structure of claim 1, wherein the gate electrode has a thickness of about 1 nanometer to about 20 nanometers.

8. The transistor gate structure of claim 1, wherein the gate structure has a width of about 0.1 micrometer to about 50 micrometers.

* * * * *